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Erbium Hydride Thermal Desorption: Controlling Kinetics

Robert M. Ferrizz

Prepared by
Sandia National Laboratories
Albuquerque, New Mexico 87185 and Livermore, California 94550

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Robert M. Ferrizz
Neutron Generator Design Science and Engineering Department
Sandia National Laboratories
P.O. Box 5800
Albuquerque, New Mexico 87185-MS0867

Abstract

Thermal desorption spectroscopy (TDS) is used to study the decomposition kinetics of erbium hydride thin films. The TDS results presented in this report show that hydride film processing parameters directly impact thermal stability. Issues to be addressed include desorption kinetics for dihydrides and trihydrides, and the effect of film growth parameters, loading parameters, and substrate selection on desorption kinetics.

Acknowledgements

Special thanks to Barry Ritchey for his help in obtaining some of the TDS data presented in this report, and for continued support and maintenance of the thermal desorption system. Thanks are also due to Saskia King for hydriding all samples studied in this report, including the well-characterized samples associated with the PCT DOEx, to Loren Espada for growing all the erbium films, to Loren and Clark Snow for providing the silicon-supported erbium films grown with different film deposition parameters, and to Len Beavis for numerous, enlightening discussions on desorption kinetics and for proof-reading this document for content.

Contents

Introduction

Thermal stability (i.e. desorption kinetics) is an important performance metric for hydride films. Thermal desorption spectroscopy (TDS) is an experimental technique well-suited for studying desorption kinetics. A detailed overview of this technique, including a description of the apparatus used in this study and preliminary thermal desorption results for erbium dihydride samples, has recently been published[1]. Experimental evidence presented in this report will show that hydride film processing parameters directly impact thermal stability. Issues to be addressed include desorption kinetics for dihydrides and trihydrides, and the effect of film growth parameters, loading parameters, and substrate selection on desorption kinetics.

Dihydrides and Trihydrides

Lundin's PCT curves for the erbium-hydrogen system[2,3] illustrate three distinctive phases: solid solution (α), dihydride (β), and trihydride (γ). Tewell and King recently published a report[4] describing loading conditions sufficient to produce erbium hydride thin films for both the dihydride (ErD_2) and trihydride (ErD_3) phase. These films were characterized using a range of techniques (XPS, AES, IBA, and XRD) to study the surface chemistry and to verify crystal phase and composition. Similar loading conditions were chosen to produce β-phase and γ-phase erbium hydrides for use in this study.

First, a number of molybdenum-supported erbium thin films (~5000A) grown by electron beam evaporation were loaded simultaneously in a PCT apparatus using the following load parameters: activation at 450 C for 30 minutes; hydriding at 450 C for 60 minutes in 10 Torr D_2. The reaction chamber was evacuated prior to cooling the freshly hydrided samples. According to Lundin's PCT curves and the IBA and XRD results published by Tewell and King, these loading conditions are expected to generate β-phase, erbium dihydride films. Note that the resultant films were blue in color, a subjective indication of β-phase ErD_2. Then, similar molybdenum-supported erbium films were loaded in the PCT using these load parameters: activation at 450 C for 30 minutes; hydriding at 250 C for 60 minutes in 150 Torr D_2. For these samples, the reaction chamber was evacuated *after* cooling to room temperature. Lundin's PCT curves and the IBA and XRD results published by Tewell and King predict that these loading conditions will generate γ-phase, erbium trihydride films. The resultant films were pink in color, a subjective indication of γ-phase ErD_3. Note that the "pink" samples obtained for thermal desorption study were derived from two similar PCT load runs.

Six thermal desorption experiments were performed for each sample set. Presented in Figure 1 are representative spectra for both the ErD_2 and (predominantly) ErD_3 samples. The sample heating rate was 0.5 C/s for each run. Erbium dihydride decomposition is observed as a sharp peak centered near 620 C. Erbium trihydride decomposition is observed as a sharp peak centered near 315 C. Note that "activated" trihydrides decompose in vacuum at temperatures as low as 200 C[4]. Therefore, the rate-limiting-step for the trihydride thermal decomposition shown here is likely sample

activation (i.e. modification of the surface oxide layer). Table 1 summarizes the results for the two major desorption peaks. Note that Redhead's method[5] was used for determining the activation energy for desorption. The E_A values for erbium dihydride decomposition presented in Table 1 are in good agreement with Beavis' reported value[6] of 61 kcal/mol.

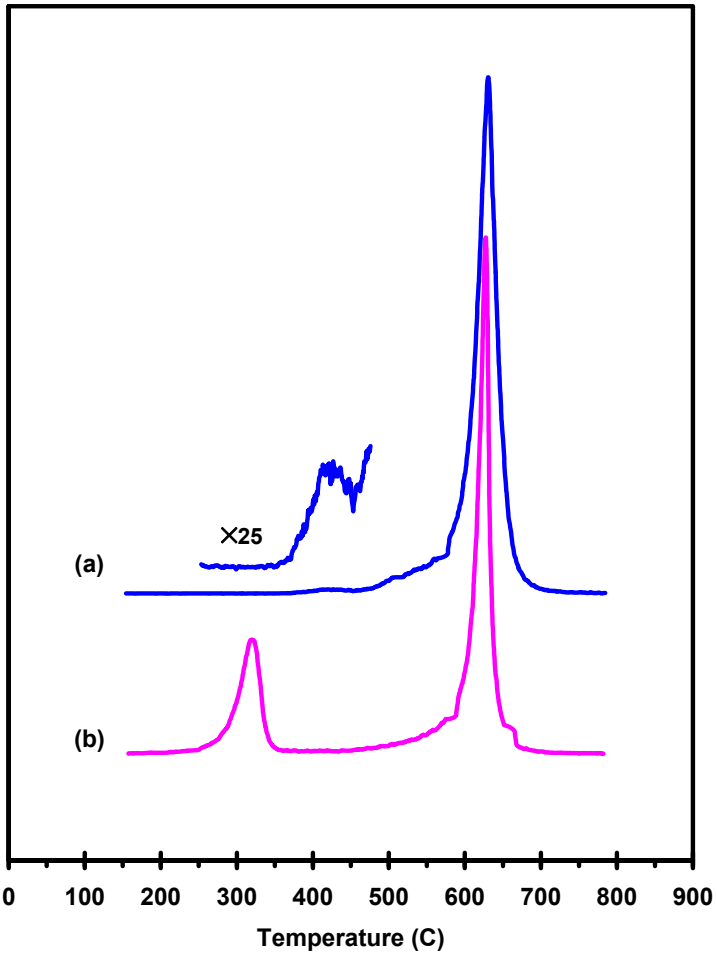

Figure 1: D_2 thermal desorption spectra (0.5 C/s) for a representative (a) "blue" ErD_2 sample, and (b) "pink" ErD_{3-x} sample.

Table 1: Average desorption peak maximum temperatures (T_P) and activation energies (E_A) for "blue" ErD_2 and "pink" ErD_{3-x} samples.

Sample	$ErD_2 \rightarrow Er$ T_P (C)	$ErD_3 \rightarrow ErD_2$ T_P (C)
ErD_2	617.5	---
95% Confidence	7.3	---
E_A (kcal/mol)	60.0	---
ErD_{3-x}	621.3	314.3
95% Confidence	13.2	19.2
E_A (kcal/mol)	60.2	39.1

Peak area analysis for the ErD_{3-x} samples yields that roughly 25% of the total amount of evolved deuterium desorbed during the trihydride decomposition peak. Therefore, it can be concluded that the pink samples had an average initial stoichiometry of roughly $ErD_{2.6}$, squarely in the middle of the 2-phase region, containing domains of both γ-phase trihydride, and β-phase dihydride.

A small peak (~2% of total D_2 desorption) is observed for the blue ErD_2 samples near 400 C. Based on recent conversations with Peter Vajda, an expert in the field of rare earth hydrides[7], this peak is tentatively assigned to octahedral site occupancy in the β-phase. Therefore, assuming a total stoichiometry (i.e. G:M) of 2.0, tetrahedral site occupancy in the "pure" β-phase would account for a stoichiometry of $ErD_{1.96}$, with the remaining 0.04 D residing in octahedral sites. Experiments designed to examine this desorption feature in greater detail are presently ongoing.

Film Growth Parameters

A preliminary study was conducted to determine the effect, if any, of film growth parameters (deposition rate and substrate temperature) on the desorption kinetics. Model samples consisting of silicon-supported erbium thin films (~5000A) grown by electron beam evaporation were chosen for this study, due to their availability and suitability for other characterization techniques. A molybdenum layer (~1000A) is deposited on the Si substrate prior to erbium deposition to act as a diffusion barrier. Two different erbium deposition parameter sets were selected, which are outlined in Table 2. It is theorized that a fast deposition rate at a low substrate temperature (sample B) will yield relatively small grains, while a slow deposition rate at high substrate temperatures (sample A) will yield relatively large grains. All samples were loaded simultaneously in a PCT apparatus using the following load parameters: activation at 450 C; hydriding at 400 C in 100 Torr D_2. Activation and load times were minimized to reduce potential Si diffusion issues. The reaction chamber was evacuated prior to cooling the freshly hydrided samples. According to Lundin's PCT curves, these loading conditions are expected to generate β-phase, erbium dihydride films.

Table 2: Erbium film growth parameters.

	Sample A	**Sample B**
Deposition Rate	10 A/s	200 A/s
Substrate Temp	500 C	200 C

Presented in Figure 2 are the thermal desorption spectra for sample A and sample B. Two runs for each sample were performed to verify repeatability. The sample heating rate was 1.0 C/s for each run. It is immediately apparent that the erbium film deposition rate and substrate temperature significantly impact the thermal stability of the subsequently loaded erbium hydride films. Table 3 summarizes the average results for each sample. Again, Redhead's method was used for determining the activation energy for desorption. Clearly, a slower deposition rate coupled with an increased substrate temperature enhances hydride thermal stability.

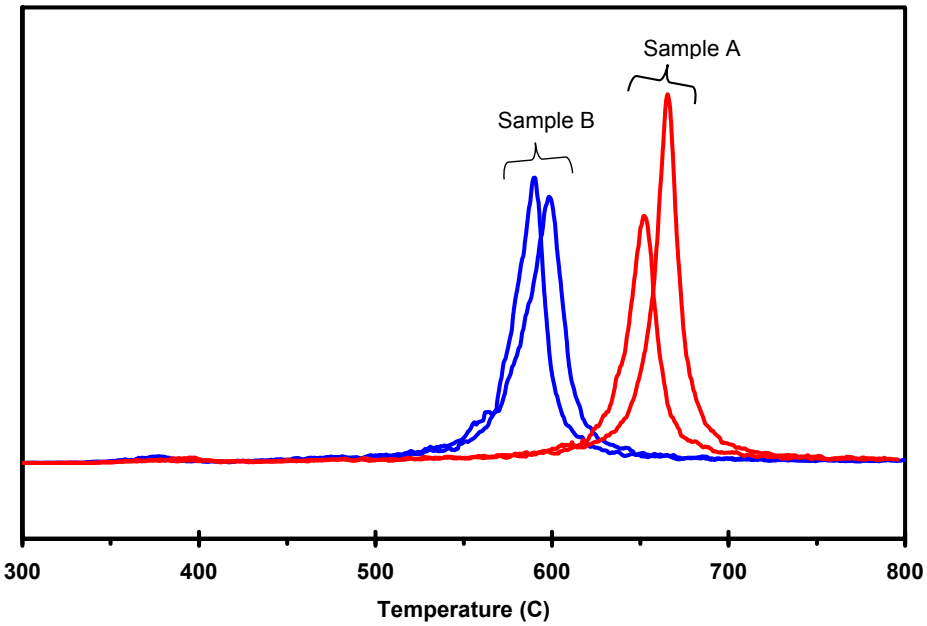

Figure 2: D_2 thermal desorption spectra (1.0 C/s) for ErD_2/Mo/Si samples A (shown in red) and B (shown in blue).

Table 3: Average desorption peak maximum temperatures (T_P) and activation energies (E_A) for samples A and B.

	Sample A ***10 A/s, 500 C***	***Sample B*** ***200 A/s, 200 C***
T_P (C)	656.5	592.5
95% Confidence	12.7	6.9
E_A (kcal/mol)	61.4	57.1

Similar to the TDS data shown in Figure 1, there is a small desorption feature observed at low temperature for both sample A (centered roughly at 395 C) and sample B (centered roughly at 375 C). These peaks account for approximately 2% of the total amount of deuterium desorption.

Loading Parameters

A comprehensive design of experiments (DOEx), led by S. King, was performed to investigate the effect of activation temperature, load temperature, load pressure, and substrate on the gas to metal ratio (G:M) of the resulting erbium hydride films. In addition to G:M results, XRD data was also gathered to determine the crystalline phases present, color observations were noted, and thermal desorption profiles were generated to study decomposition kinetics. This section will focus on the TDS results for the molybdenum-supported erbium hydride films studied as part of this DOEx.

Briefly, the samples studied in this DOEx consisted of erbium films deposited on molybdenum and kovar substrates. The samples were activated at 300 C, 400 C, or 500 C, and then hydrided at 300 C, 450 C, or 600 C, in 10 Torr, 150 Torr, or 500 Torr of a hydrogen/deuterium gas mixture. Two samples from each load run were submitted for G:M analysis, and one or two samples from most load runs were thermal desorbed at a rate of 0.5 C/s. The experimental matrix, peak maximum desorption temperatures, and G:M results are summarized in Table 4.

Table 4: DOEx controlled factors and response variables for Mo-supported erbium hydride films.

Run #	Act Temp (C)	Load Temp (C)	Load Press (Torr)	$T_{PEAK\ MAX}$ (C)	G:M
1	300	300	10	582.4	2.160 ± 0.035
2	300	300	500	551.4	2.389 ± 0.082
3	500	300	500	559.3	2.423 ± 0.078
4	300	600	500	585.1	1.956 ± 0.032
5	500	600	500	695.3	2.018 ± 0.023
6	400	450	500	575.1	2.000 ± 0.017
7	400	300	150	587.6	2.027 ± 0.027
8	400	450	150	599.9	1.968 ± 0.005
9	500	450	150	589.0	1.985 ± 0.009
10	400	600	150	592.3	NA
11	300	450	150	580.0	2.005 ± 0.007
12	500	300	10	NA	2.066 ± 0.014
13	300	600	10	603.3	1.947
14	500	600	10	NA	1.931
15	400	450	10	NA	2.005

As expected, G:M trends with load temperature and pressure as predicted by Lundin's erbium-hydrogen isotherms. To summarize, high temperatures and low pressures favored smaller G:M values (while still producing β-phase erbium dihydride), while low temperatures and high pressures favored higher G:M values (primarily β-phase, with smaller domains of γ-phase ErD_3 in some instances).

Figures 3, 4, and 5 illustrate the TDS results presented in Table 4, with load temperature held constant for each figure. In Figure 3, desorption peaks are observed spanning 300 to 400 C, and again at 500 to 650 C. The lower temperature peaks are due to erbium trihydride decomposition (γ-phase to β-phase transition), while the higher temperature peaks are due to erbium dihydride decomposition. The presence of erbium trihydride in the TDS results for runs 1, 2, and 3 is consistent with the G:M values and XRD results (not shown) for these same runs. Peak area analysis of the thermal desorption spectra yields G:M values of 2.18, 2.26, and 2.32, respectively, for runs 1, 2, and 3. Note that the samples exhibiting trihydride domains were all loaded at 300 C and primarily high pressures (500 Torr H_2/D_2), conditions that are expected to result in γ-phase trihydride according to Lundin's erbium-hydrogen isotherms. Furthermore, note

that the samples which possess trihydride decomposition peaks tend to exhibit dihydride decomposition at relatively lower temperatures. For example, the dihydride decomposition peak for runs 1, 2, and 3 is centered at an average of 561.6 C, while this same peak is centered at an average of 584.5 C for runs 7 and 12. This suggests that the presence of trihydride domains decreases the thermal stability of the β-phase dihydride.

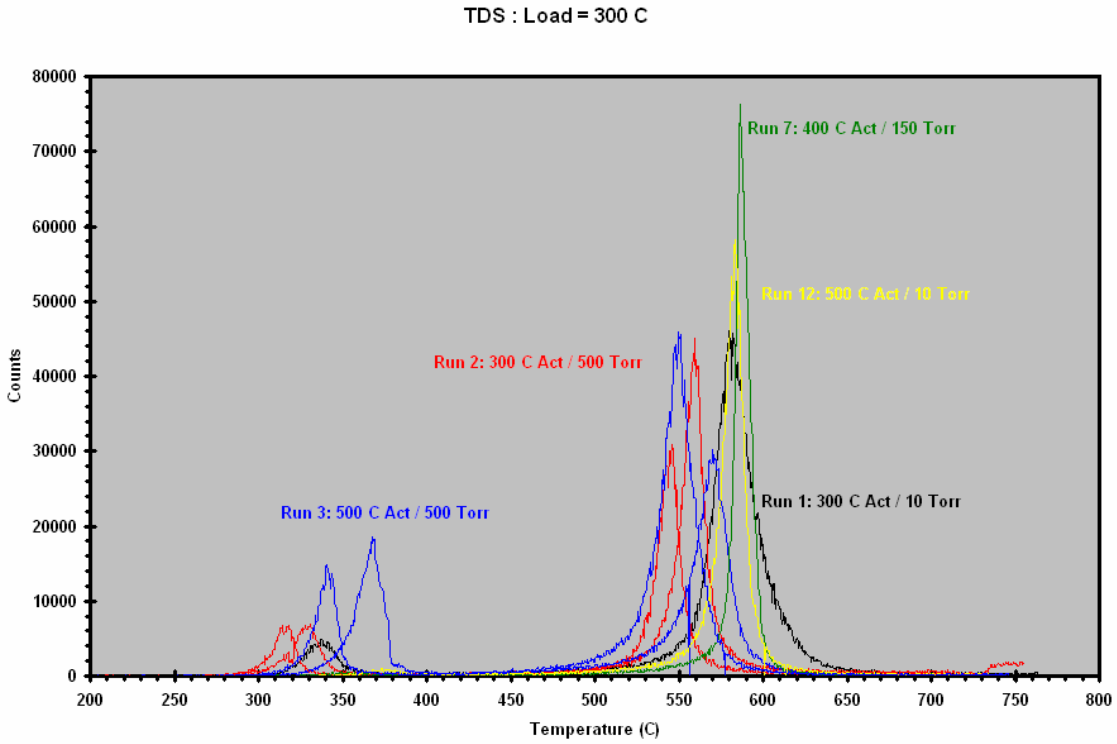

Figure 3: Thermal desorption spectra (0.5 C/s) for DOEx samples (Load = 300 C).

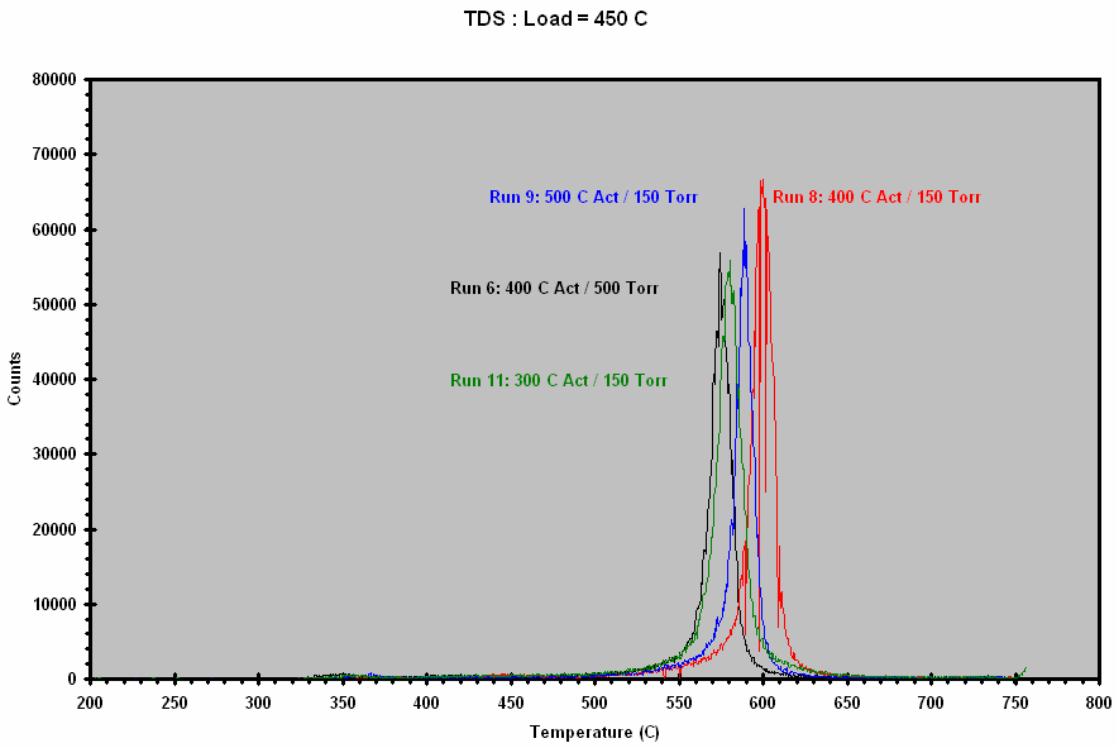

Figure 4: Thermal desorption spectra (0.5 C/s) for DOEx samples (Load = 450 C).

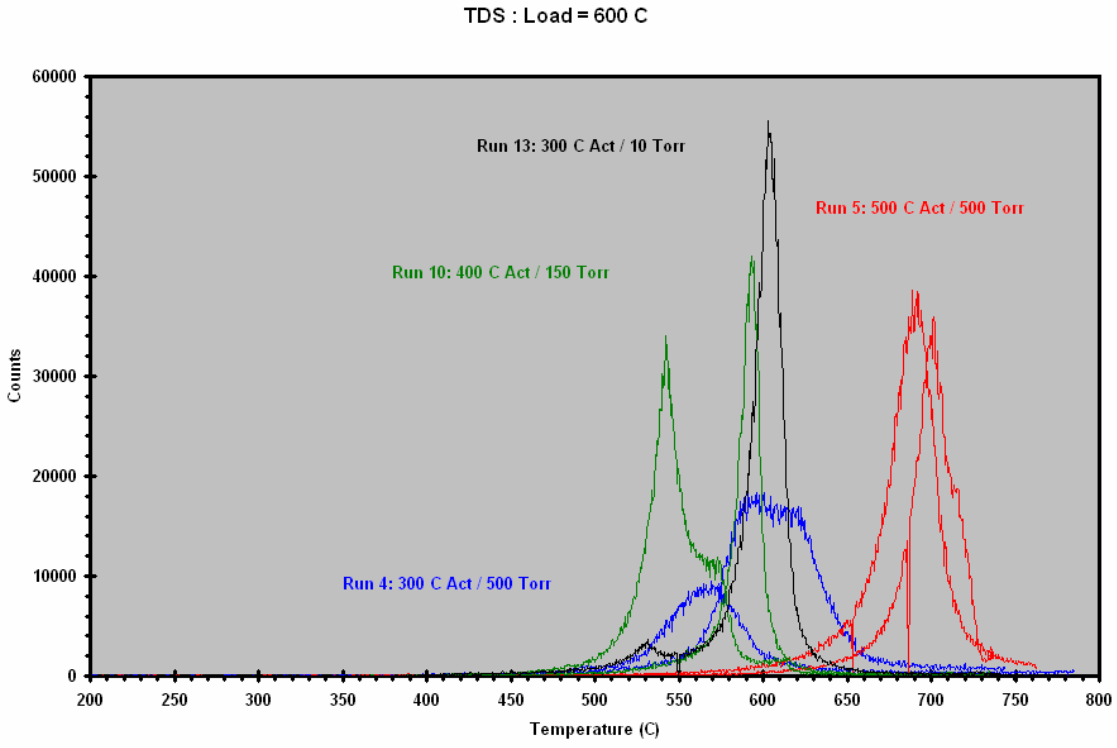

Figure 5: Thermal desorption spectra (0.5 C/s) for DOEx samples (Load = 600 C).

The TDS results for samples loaded at 600 C are presented in Figure 5. Relative to the desorption peaks for samples loaded at lower temperatures (see Figures 3 and 4), the desorption peaks for samples loaded at 600 C are, in general, more broad, at times seeming to exhibit a two-peak structure for dihydride decomposition. The TDS results for run 5 (activation at 500 C, load at 600 C/500 Torr) are particularly interesting, as the dihydride decomposition peak is centered at an average of 695 C, a value over 100 C greater than that observed for nearly all the other samples. Redhead analysis yields an activation energy for desorption of 65.4 kcal/mol, the largest value yet observed for erbium dihydride decomposition. Note that the TDS experiments were performed twice for run 5 samples, with consistent results, verifying that the observed high temperature desorption peak is not an anomaly due to experimental error. The enhanced thermal stability observed for run 5 is presently under further investigation, as this sample has exciting implications for applications involving hydride films in vacuum tubes, where high temperature "bakeouts" are used to minimize impurity levels in the vacuum envelope.

In Figure 5, note the contrast in peak maximum desorption temperature for runs 4 and 5. The only difference between these samples is the activation temperature. This suggests that, in addition to loading conditions, the activation conditions are critical for controlling the desorption kinetics of erbium hydride thin films.

An important feature of Figure 5 that is not readily apparent is that there are no low temperature desorption peaks observed for any sample loaded at 600 C. The TDS data below 400 C is completely flat, with intensity only appearing above 400 C as a low temperature shoulder to the high temperature dihydride decomposition peak. Assuming that the absence of a low temperature desorption peak, which is present for all other samples studied for this report, is due to a lack of octahedral site occupancy, this means that samples loaded at 600 C will tend to have lower G:M values than those loaded at lower temperatures. It is speculated that this is due simply to the fact that octahedral site occupancy is "pumped off" when the load run is completed and the hydrogen/deuterium gas is removed prior to sample cooling, resulting in a "pure" β-phase composition consisting only of hydrogen at tetrahedral sites in the erbium hydride lattice. This theory is consistent with the G:M values presented in Table 4 for samples loaded at 600 C. Note that, within experimental error, all 600 C-loaded samples have stoichiometries of $ErD_{2.0}$ or less. An additional explanation for the lack of octahedral site occupancy is that high temperature loading may promote the formation of large oxide particles in the bulk, rather than oxygen atoms at tetrahedral sites. Therefore, less hydrogen would be displaced from tetrahedral sites, resulting in fewer octahedral sites being occupied. Minimizing G:M through reducing or eliminating octahedral site occupancy would be a complementary effect to the thermodynamic trend evident in Lundin's isotherms, which predicts that high temperatures and low pressures favors a lower β-phase G:M ratio during the loading process. The potential for controlling octahedral site occupancy via thermal desorption has significant implications with respect to controlling loading stoichiometry, and is a focus of ongoing investigations.

It is curious that this low temperature desorption peak is observed at all, for any of the samples studied in this report, as most samples were loaded at 450 C or greater, temperatures greater than that required to desorb this hydrogen species under UHV conditions. Clearly, at elevated temperatures, the quality of the vacuum environment under which the hydride films are exposed to has a significant impact on the desorption kinetics. A possible explanation is that the pressure driving force[1,8] for desorption is reduced or nil when H_2 is present in the background at the moderate vacuum levels found in a typical loading apparatus. Also, there is significant evidence[9,10] that suggests that the surface oxide stabilizes the hydride (i.e. increases the decomposition temperature), and it is likely that the stabilizing influence of the surface oxide is a function of the vacuum environment (i.e. UHV versus loading apparatus). This issue can potentially be addressed by performing thermal desorption experiments under less-than-ideal vacuum conditions, and by carefully controlling the reactivity of the hydride surface through the use of catalysts or sputtering, for example.

For a statistical analysis of the TDS results, refer to the upcoming report of S. King's PCT DOEx. A brief summary of the major trends are as follows. First, higher G:M correlates to lower peak maximum desorption temperature, for the most part. Second, there was weak to no correlation between load pressure and desorption temperature. However, there was a strong correlation between activation and load temperature and desorption temperature, with higher temperatures for both processes tending to increase the thermal stability of the resulting hydride films.

At present, TDS experiments have not been performed for a large majority of the kovar-supported erbium films that were also studied as part of the PCT DOEx detailed above. However, the TDS results for run 3 are quite interesting, and are presented below as Figure 6. Note that the kovar and Mo-supported erbium films were loaded simultaneously, so that the same activation and load conditions are used for each sample, the only difference being the underlying substrate. Clearly, the support has a huge role in determining the stability of the trihydride phase. Please refer to the upcoming PCT DOEx report for additional comments on kovar-supported erbium films, including diffusion issues at the kovar-erbium interface.

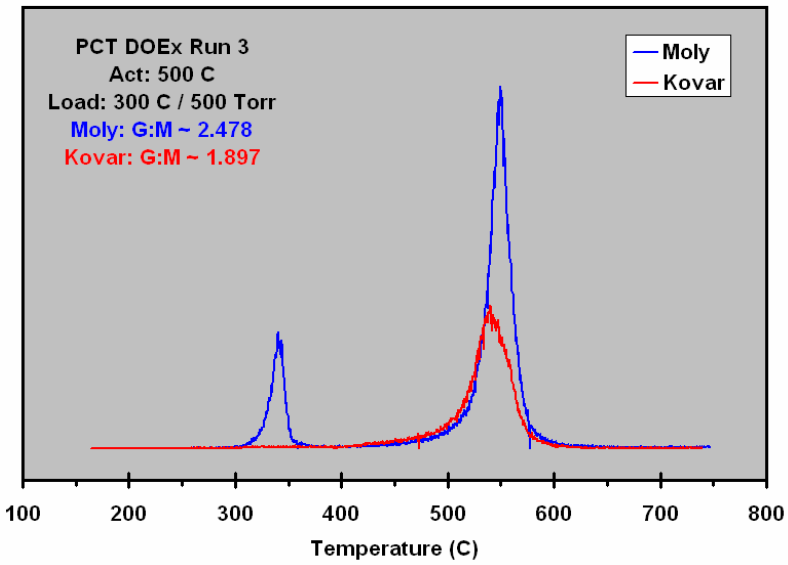

Figure 6: Thermal desorption spectra (0.5 C/s) for erbium hydride films (DOEx run 3) supported on molybdenum (blue) and kovar (red) substrates.

Conclusions

A major conclusion from this TDS study is that desorption kinetics can be controlled by processing parameters. Both film growth and hydriding parameter led to significant changes in the activation energy for hydride decomposition. Particularly promising evidence for enhancing film stability were the erbium hydride films loaded at 600 C after a high temperature activation step. The fundamental basis for changes in desorption kinetics will require further study and complementary analytical techniques. Likely, film stress and surface chemistry are both critical factors. Secondly, it is possible to generate trihydride domains for Mo-supported erbium films for "reasonably obtained" processing parameters, and that care must be taken to avoid such conditions, as apparently the historical presence of trihydride leads to erbium dihydride films of poorest thermal stability. Next, extraction of samples from the loading apparatus is critical. Depending on loading temperatures and pressures and the cooling/evacuation protocol, it is possible to produce erbium trihydride films, or erbium dihydride films with minimal low temperature (octahedral?) hydrogen species. Areas for future study were highlighted throughout the report, including the conclusive identification of octahedral site occupancy in the thermal desorption spectra of ErD_2 samples. Finally, a general, fundamental understanding of the factors that control decomposition kinetics will likely result in a range of hydride films with enhanced thermal stability. For certain applications, this knowledge may "open the door" to new materials with excellent mechanical and helium retention properties that were previously unavailable due to insufficient thermal stability.

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